Novel Dispersed-Phase Catalytic Approach to Coprocessing

by

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ABSTRACT

The Pittsburgh Energy Technology Center (PETC) is currently testing a new process concept for catalytically coprocessing a mixture of coal and petroleum-derived residual oils. The catalyst used in this process is molybdenum added directly to the reactor as an aqueous solution. Recent results are presented for product yield structure obtained in a 1-liter semibatch reactor. A discussion is also given for some recent findings obtained from coprocessing studies in a 1-liter continuous reactor system.

An important economic advantage in using this process can be gained if recovery of the dispersed catalyst from the product residue is demonstrated. A discussion is provided of an approach to catalyst recovery that does not require complicated processing steps and uses relatively inexpensive reagents. Results are presented from preliminary testing of the recovery process that indicate it is feasible to efficiently recover the catalytically active material for reuse in the process.

INTRODUCTION

The rapid consumption of conventional light petroleum reserves and the increasing need to refine lower quality petroleum feedstocks have recently prompted serious consideration of technology for coprocessing coal with petroleum residual oils or heavy bitumens. Coprocessing is attractive as a possible route for introducing the processing of coal in an evolutionary manner into existing refinery infrastructures without immediately incurring the large capital investment associated with other coal liquefaction alternatives.

Previous coprocessing experiments conducted at PETC in a noncatalytic operation (Lett and Cugini, 1986) have led to several conclusions. First,

coal is capable of enhancing demetallation of the petroleum solvent stream. The demetallation mechanism appears to be an adsorption process whereby the metals are adsorbed onto the surface of the coal remaining undissolved at the reaction conditions. Second, distillate yields in coprocessing are larger than would be predicted from linear addition of the distillate yields based on independent processing of the coal and petroleum-derived solvent. Two factors appear to be responsible for this result. First, the petroleum-derived solvent can act as a hydrogen donor solvent (although a poor one) for the coal; and second, coal enhances the conversion of the oil through the catalytic effects of the inorganics in the coal, primarily pyrite. While these are positive results obtained in the noncatalytic coprocessing approach, the liquid product yields are too low and would not appear to justify a noncatalytic approach to coprocessing.

In our preliminary catalyst-screening studies, we evaluated a single-stage approach to catalytic coprocessing. While two-stage coprocessing has merits, mainly dealing with coal's inherent ability to remove metals from the petroleum and thereby reduce second-stage catalyst aging, the use of a supported catalyst at any point increases the difficulty of ultimately recovering the expensive metals used in formulating the catalyst. A dispersed-phase catalyst would facilitate recovery of the active metals. Also, the most active materials for single-stage upgrading have been finely dispersed catalysts, either supported or unsupported. Therefore, we chose a dispersed-phase catalyst for use in single-stage coprocessing. The form chosen was a water-soluble salt, specifically ammonium molybdate. This material is readily available, and the molybdenum in a catalyst recovery process is readily recovered as ammonium molybdate.

EXPERIMENTAL RESULTS AND DISCUSSION

Batch Operation

Catalyst (additive) screening tests were initially conducted in 42-mL microautoclave reactors. The objective of these tests was to identify potential active catalysts for coprocessing. The catalysts (additives) tested include aqueous ammonium heptamolybdate, hydrogen sulfide, hydrogen sulfide/water, and pyrite. These catalysts were tested at typical coprocessing reaction conditions; i.e. 435°C, 1200 psig cold H_2 charge, a residence time of 1 hour, and a 70 wt% concentration of Maya ATB with 30 wt% Illinois #6 coal. Analyses of the major thermophysical properties of Maya ATB and Illinois No. 6 coal are presented in Tables 1 and 2.

The products from the batch tests were removed from the reactors and separated into soluble and insoluble fractions. The product yield distributions for the catalyst-screening tests are shown in Figure 1. The molybdenum catalyst was the most active catalyst tested. The use of 0.1% Mo (based on total feed slurry) as aqueous ammonium molybdate resulted in the highest heptane-soluble-oil yield and lowest pitch (THF-insolubles) yield. The use of pyrite or H_2S resulted in an increase in conversion, with the pyrite being the more active of the two additives. Addition of water to the hydrogen sulfide system did not appreciably alter the product yield distribution.

The aqueous ammonium heptamolybdate catalyst precursor was also tested in a semibatch 1-liter autoclave reactor. The reaction conditions in the semibatch autoclave were similar to those in the microreactor with the exception that a flow-through gas was used. The gas rate was 4 scf of H_2 per hour. The feed charge consisted of 500 grams of coal/oil slurry.

The objective of these batch 1-liter tests was to determine the effect of scaling up from batch microreactor tests to semibatch operations (batch liquid, flow-through gas) on conversions and product distributions. These tests were conducted in both catalytic and noncatalytic systems. Figure 2 presents a comparison of the microreactor and 1-liter autoclave reactor product yields from coprocessing. The pitch conversion was similar in both cases. The major difference in the two systems was observed in the asphaltene (defined as heptane-insoluble/THF-soluble fraction) and oil (defined as heptane-soluble) yields. Apparently, the asphaltenes are converted to oil to a much larger extent in semibatch 1-liter reactors than in microreactors. This is observed in both catalytic and noncatalytic systems.

The work-up procedure for the semibatch system includes a distillation step. The total oil product is distilled after the heptane insolubles have been extracted. The distillation step employed a modified ASTM D1160 procedure. Figure 3 includes the results from the distillation of the heptane-soluble products for the semibatch catalytic and noncatalytic runs. The effect of the catalyst is most pronounced on the yield of distillable (C_5-950°F) oil. A duplicate run for the catalytic case is also presented in Figure 5.

Continuous Unit Operation

The ultimate objective was to develop a dispersed-catalyst system capable of being used in a single-stage continuous operation. Continuous catalytic coprocessing experiments were performed in a computer-controlled 1-liter bench-scale continuous unit shown in Figure 4. A mixture of 30 wt% coal ground to 200 x 0 mesh and 70 wt% Mayan atmospheric tower bottoms (ATB - 650°F+ boiling material) was injected along with an aqueous ammonium heptamolybdate stream and a hydrogen and hydrogen sulfide gas stream (the H_2S insures that the molybdenum has access to adequate sulfur to be converted to its sulfide form) into a preheater and reactor combination maintained at 2500 psig. Earlier microautoclave studies demonstrated the need for a gradual heat-up of the feed slurry (Cugini and Lett, 1987). Temperature staging of the preheater and reactor was used to provide this gradual heat-up in a continuous system. The residence time in the preheat zone is approximately 20 minutes. The operating conditions used for these runs were the following:

Reactor Temperature:	435°C
Pressure:	2500 psig
Catalyst Feed Concentration	0.003
(g Mo/g coal + oil)	
Gas Feed Concentration (vol %):	97% H_2; 3% H_2S
Space Velocity:	0.75 hr^{-1}
Gas Feed Rate:	10 scfh

Slurry Feed Rate: 250 g/hr

The run was continuously operated for 100 hours with no operational
problems. The separation scheme used to analyze product distributions was
similar to that used for the semibatch 1-liter products. The product gases
were sampled using gas burettes and analyzed by gas chromatography. The
average material balance over the course of the 100 hours was 96.8%. Table
3 presents product distributions from a 12-hour material balance period. A
high yield of distillable product is obtained with the use of catalyst in
the system. The insoluble product yield is low, which indicates high
conversion of coal to soluble products. The hydrogen consumption is 3.0 wt%
of total feed slurry.   Coupled with the yield of 80.1 wt% of C_5-950°F
product, the hydrogen utilization efficiency is 26.7 lb distillate per lb
H_2.

Catalyst Recovery

To improve the feasibility of PETC's coprocessing scheme, it was felt that a
catalyst recovery scheme should be developed. The use of an unsupported
molybdenum catalyst would facilitate catalyst recovery because there would
be no interferences from the support material, and the recovered form of the
catalyst could readily be reused as a catalyst in the process.

The recovery scheme that is being developed is similar in concept to Exxon's
recovery scheme for coal liquefaction catalysts (Francis and Veluswamy,
1983). The coprocessing residue is oxidized to separate the carbon from the
catalyst-containing mineral matter and to convert the metals in the mineral
matter to their oxide form. The resultant ash is extracted with an alkali
solution to first solubilize the molybdenum and then solubilize the nickel
and vanadium.

An experimental program has been initiated to test the feasibility of this
recovery scheme. The first stage of the program was to recover molybdenum
from a mixture of coal ash and added metal oxides in a ratio to represent
the mixture from a calcined stream of a residue from coprocessing 30%
Illinois No. 6 coal and 70% Maya ATB. The composition of this mixture is
presented in Table 4. The mixture was calcined at 700°C to allow for high-
temperature interactions between the metals that might occur during the
calcining step. The mixture was then extracted with ammonium hydroxide at a
series of pH's and temperatures. The results of three catalyst recovery
tests are also presented in Table 4. These results indicate that on model
systems it is possible to extract 97% of the molybdenum with little
contamination by vanadium.   More tests are planned to optimize the
extraction method on actual coprocessing residues.

CONCLUSIONS

The approach taken to catalytically coprocess a mixture of coal and
petroleum-derived residual oil in a single-stage process has been
demonstrated successfully. A high-activity unsupported catalyst has been
developed that is capable of enhancing coal conversion and distillate

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yields. Activation of the catalyst has been demonstrated successfully for batch and continuous operations. In a moderate-severity mode of operation, 87 weight percent of the 950°F+ organic material in the slurry feed (Maya ATB and Illinois No. 6) is converted. The hydrogen consumption is about 3 weight percent of the feed.

The catalyst precursor used in this process is ammonium heptamolybdate added directly to the reactor as an aqueous solution. Preliminary results from model compound studies for recovery of the catalyst indicate that a significant fraction of the catalyst (97 percent) can be recovered for reuse.

FUTURE PLANS

The results obtained to date reflect early findings of scale-up from batch to continuous operations of catalytic coprocessing in a single-stage process. The catalyst activation sequence, although successful, has not been optimized. Since the pretreatment of the catalyst played a key role in the ultimate activity of the catalyst, several interdependent investigations will be pursued: (1) the time and temperature effects of preheating in the continuous mode of operation; and (2) the effect of adding promoters to the ammonium molybdate catalyst on coprocessing performance.

A research effort will continue to develop a recovery process for the spent catalyst in the coprocessing residual products. Efforts to date indicate that recovery of catalyst from calcined residues can be performed at very high levels of recovery via an extraction process. Coprocessing residual products will be subjected to calcination and catalytic metals recovery by leaching with an ammonium hydroxide solution. The goal set for the recovery process will be greater than 97 percent recovery of the molybdenum catalyst.

ACKNOWLEDGMENTS

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Table 1

ILLINOIS NO. 6
(Burning Star)

Proximate Analysis, wt%
     (as-received)

     Moisture.. 4.2

     Volatile Matter..................................... 36.9

     Fixed Carbon.. 48.2

     Ash... 10.7

Ultimate Analysis, wt%
     (moisture-free)

     Carbon.. 70.2

     Hydrogen.. 4.8

     Nitrogen.. 0.9

     Sulfur.. 3.1

     Oxygen (diff.)...................................... 9.9

     Ash... 11.1

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Table 2

MAYA ATB
(650°F+)

</div>

Ultimate Analysis, wt%

     Carbon.. 84.5

     Hydrogen.. 10.6

     Oxygen.. 0.3

     Nitrogen.. 0.5

     Sulfur.. 4.0

     Ash... 0.1

Ni(ppm).. 70
V (ppm).. 370

950°F-, vol%... 30
ASTM D1160

Heptane Insols, wt%.. 20
ASTM D3279

Table 3

PRODUCT YIELDS AND CONVERSIONS -- (CAT-8-2)

Yield Structure

Component	Coal + Heavy Oil (Ash-Free) Weight Percent	950°F (Ash-Free) Weight Percent
C_1-C_4	5.1*	6.9
C_5-950°F	80.1	74.5
950°F+	6.9	8.7
Heptane Insolubles	3.7	4.6
Non-Hydrocarbon Gases	7.2*	9.2
Hydrogen Consumption	-3.0	-3.9

Conversions (Ash-Free Basis)

Component	Weight Percent
950°F+	87
THF Insolubles	95
Heptane Insolubles	92

*Estimated from tail gas sampling.

Table 4

Model Compound Extractions

Model Mixture

Component	Weight Percent
Coal Ash	92.8
V_2O_5	2.8
NiO	0.1
MoO_3	4.3

Molybdenum Recovery

Test	Wt% Mo Recovered As Molybdate	Wt% of V Recovered with Molybdate
1	75	2
2	95	5
3	97	22

100

80

60

Yield, wt%

40

20

0

Maya ATB   70%
Illinois No. 6   30%
Pressure   2500 psig
Temperature   435°C
Residence Time   1 hr

☐ No catalyst
■ 0.1% Mo
▨ 5% hydrogen sulfide
▧ 5% hydrogen sulfide + 1.0% water
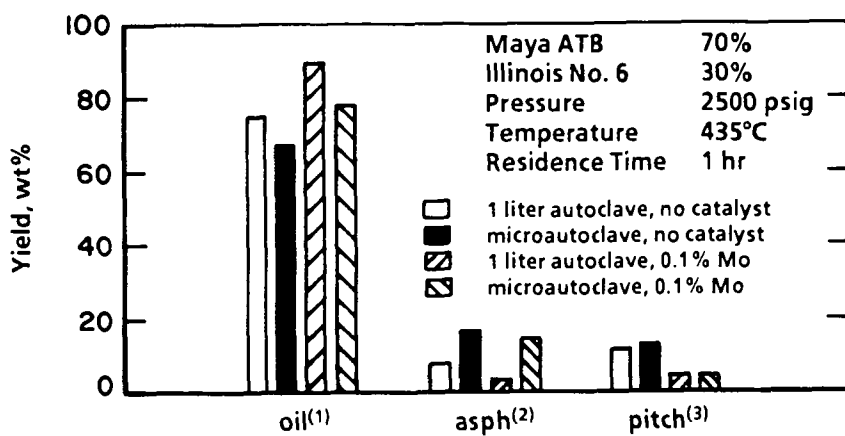◩ 10% pyrite

oil(1)   asph(2)   pitch(3)
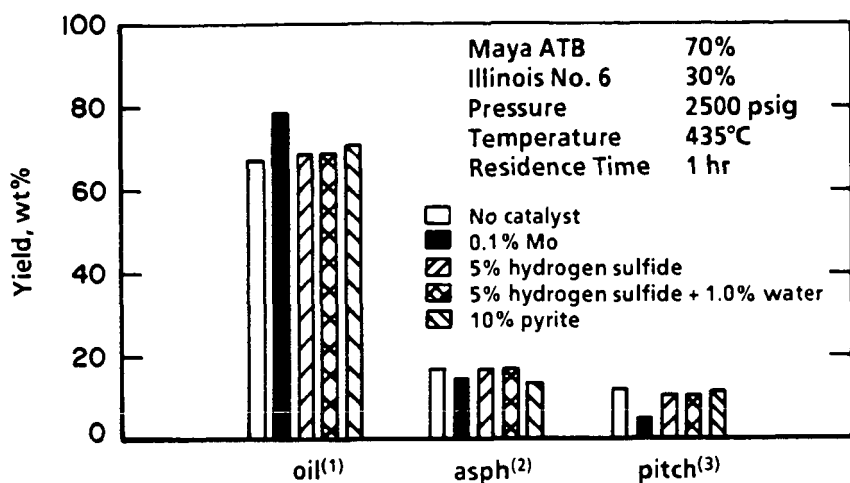
(1) heptane solubles
(2) heptane insoluble/THF soluble
(3) THF insolubles

Figure 1.

MICROAUTOCLAVE PRODUCT YIELDS

Figure 2.

COMPARISON OF MICRO- AND 1 LITER-AUTOCLAVE
REACTOR SYSTEMS

(1) heptane solubles
(2) heptane insoluble/THF soluble
(3) THF insolubles
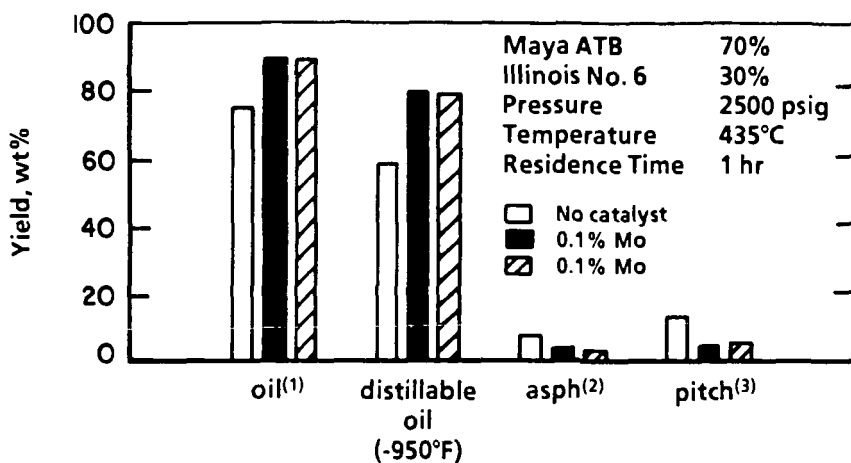
(1) heptane solubles
(2) heptane insoluble/THF soluble
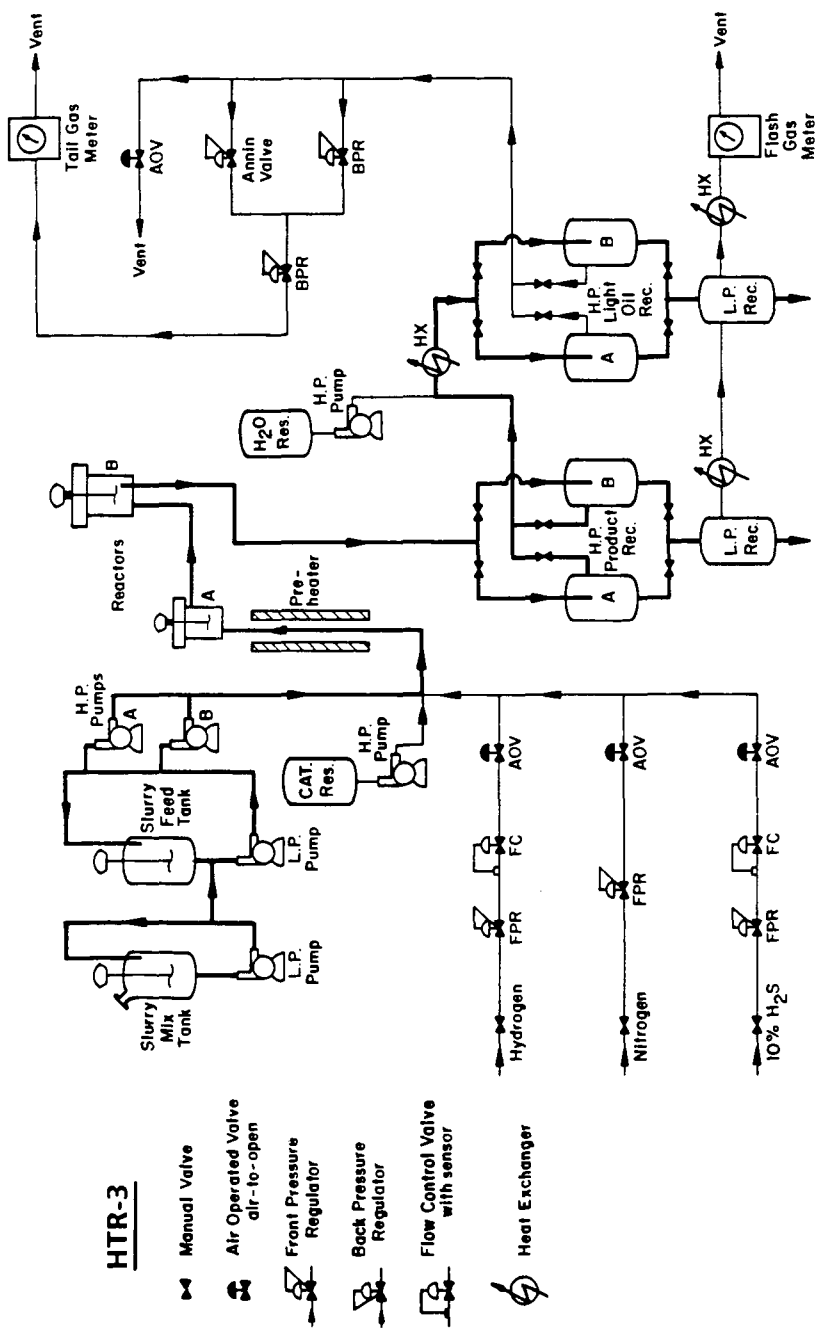(3) THF insolubles

Figure 3.

BATCH 1 LITER AUTOCLAVE YIELDS

Figure 4. Schematic of Bench-Scale Continuous Coprocessing Unit

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